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ORIGINAL ARTICLE

Computational study of the molecular hydrogen physisorption in some of the corannulene derivatives as a carbon nanostructure

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Carbon nanostructure

Abstract Substitution of the peripheral H atoms in the corannulene molecule as a carbon nanostructure by OH, CH_3, NH_2 and NO_2 groups on the molecular hydrogen physisorption was evaluated at MP2/6-31G(d) level of theory. Two orientations of hydrogen were used on the concave and convex sides of corannulene. It was seen that binding to the concave face is favored relative to the convex face. The average binding energy was calculated and corrected for the basis set superposition error (BSSE) using the counterpoise method. Results showed that binding energy varies depending upon the site and side of absorption. The electronic density, charge transfer and spatial prohibition of the substituted groups affects the binding energy. The increment of the electronic density because of the substitution of electron donor groups facilitates hydrogen adsorption and leads to larger binding energies than when H atoms are substituted by electron acceptor groups. Substitution of H atoms with each of the considered groups leads to decreasing of the HOMO–LUMO energy gap and so decreasing of the kinetic stability and increasing of the reactivity. The energy gap and binding energy for corannulene derivatives decreases in the order of: $CH_3 > OH > NH_2 > NO_2$.

1. Introduction

Hydrogen has received growing attention in the area of research because it can be refreshed and is environmentally friendly. The suitable hydrogen storage materials should store hydrogen in high volumetric and gravimetric densities with fast kinetics as well as desirable thermodynamics. Therefore, improving new materials for effective and safe hydrogen storage is a very important problem, as the 2010 United States Department of Energy goal for vehicular applications is storage of 6.0 wt.% hydrogen, with a goal of 9.0 wt.% hydrogen by 2015 [3,16,19,39].

Considerable efforts are devoted toward developing new storage materials. There are different advanced hydrogen storage materials including metal hydrides, polymers, metal organic framework, covalent organic framework, carbon-based nanomaterials and clathrates. In metal hydrides, the

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hydrogen uptake capacity is low and the hydrogen adsorption on metal hydrides is chemisorption, and thus desorption of hydrogen occurs at temperatures above 500 K [7,28,36]. In organometallic materials, hydrogen adsorption is physisorption but they have low density and high surface area and are porous materials. Low hydrogen uptake at room temperature is the main disadvantage of using them as adsorbents [26,30]. Carbon-based materials, including nanotubes, nanofibers, nanoscrolls, buckybowls, activated carbon materials and graphene sheets have been analyzed experimentally and theoretically [5,6,12,24,25,31,33–35,40]. However, as a result of the weak interactions between H_2 and pure carbon, these materials do not show sufficient storage capacity for commercial use under room temperature working conditions. Adjustment of C-based materials to enhance interactions between H_2 and absorbents and then to enhance the physisorption of H_2 is essential for development of hydrogen storage [1,9,18,29].

Corannulene is one of the simplest curved 2D carbon nanostructures and can be represented as one third of a C_{60} fullerene molecule with hydrogen termination that was synthesized long ago by Barth and Lawton in 1966 [2]. But its importance was realized only after the discovery of C_{60} fullerene. Naturally, this compound and its derivatives have drawn considerable interest among synthetic and computational chemists. Corannulene is commercially available, relatively easy to synthesize and has a small curvature, so one can compare it with fullerene. It has a bowl geometry and open ended structure unlike fullerenes. Moreover, both concave and convex surfaces of corannulene molecule with different electron density distributions are exposed to react with a hydrogen molecule [1]. Beside corannulene and derivatives, there are new synthesized carbon-structures including aromatic fused-rings that could be potentially evaluated for hydrogen storage [17,20–23].

Recently, hydrogen adsorption in corannulene-based materials was evaluated by Zhang et al. [39]. They have shown that corannulene has potential advantages as hydrogen storage material over planar graphite and even carbon nanotubes. Also, in lithium doped corannulene, lithium atoms are more stably doped over the six-member rings than over the five-member ring of corannulene with the concave side more favorable than the convex side of corannulene for doping. The doping of lithium atoms enhances the hydrogen adsorption due to three factors: Lithium-doped corannulene complexes have higher dipoles, the interaction between the lithium atom and hydrogen is stronger than the interaction between carbon atom and hydrogen and the doping of lithium atoms provides more space in the doping complexes for hydrogen adsorption [38]. Rellian-Pineiro et al. have considered the interaction of corannulene with alkali cations by DFT and MP2 methods (Rellán-Piñeiro et al., [27]). Interaction of Hydrogen molecules with some of the carbon nanostructures such as C_{60}, C_{36} and several B and Be-doped carbon nanostructures was studied by the MP2 method [31]. Banerjee et al. have shown that for interaction of alkali and alkaline earth metal ion doped corannulene molecules with dihydrogen, the smaller and larger size ions show higher binding energy on the convex and concave sides, respectively. Also, the clean surface of the molecule interacts with hydrogen very weakly and the binding strength is significantly improved after decorating the molecule by alkali or alkaline earth metal ions [1]. Hydrogenation and fluorination of the corannulene have been carried out by Santos et al. [32]. They have shown that the hydrogenation or fluorination significantly changes the HOMO−LUMO (H−L) energy gap of the system and strongly depends on the concentration and the position of the incorporated F atoms. Also, the fluorinated corannulene systems are considerably more stable than their hydrogenated analogs.

In this study, we have focused on hydrogen adsorption in some of the corannulene derivatives and investigated the effect of different substituent groups in corannulene on the hydrogen adsorption by using the MP2 method. We have used a different route to vary the electronic density of the corannulene by adding electron donor and electron acceptor groups to corannulene. Interaction energy with respect to BSSE correction was calculated and the best corannulene derivative was assigned for hydrogen adsorption. We expect that the present characterization can help to synthesize these derivatives of corannulene and to design suitable materials to store hydrogen.

2. Computational details

2.1. Ab initio calculations

Geometry optimization of all structures were done at MP2/6-31G(d) level of theory to account for weak Van der Waals forces that are responsible for the hydrogen molecule-corannulene derivatives interaction based on physisorption interaction. MP2/6-31G(d) frequency calculations were performed to ensure that the molecular system was at a local minimum. For evaluation of interaction of H_2 and corannulene derivatives, two orientations of hydrogen are used (perpendicular

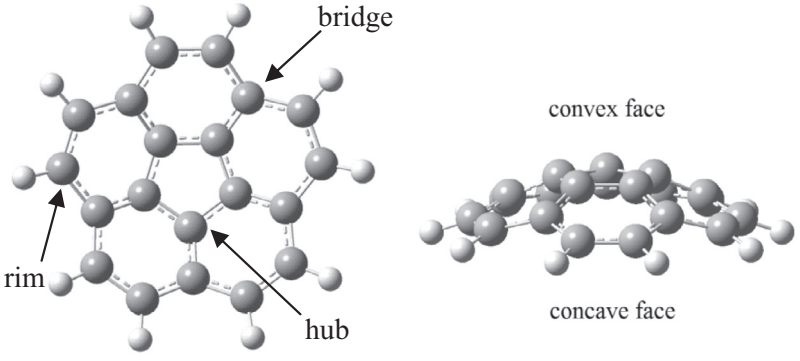

Figure 1 Optimized bowl-shaped structure of the corannulene molecule ($C_{20}H_{10}$) and different carbon atoms.

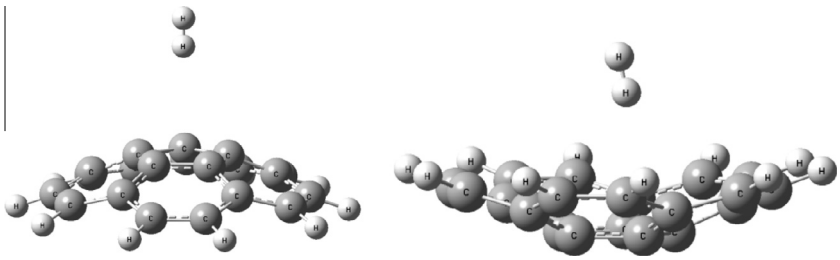

Figure 2 Optimized corannulene molecules with perpendicular H_2 physisorbed on the convex side (left) and the concave side (right).

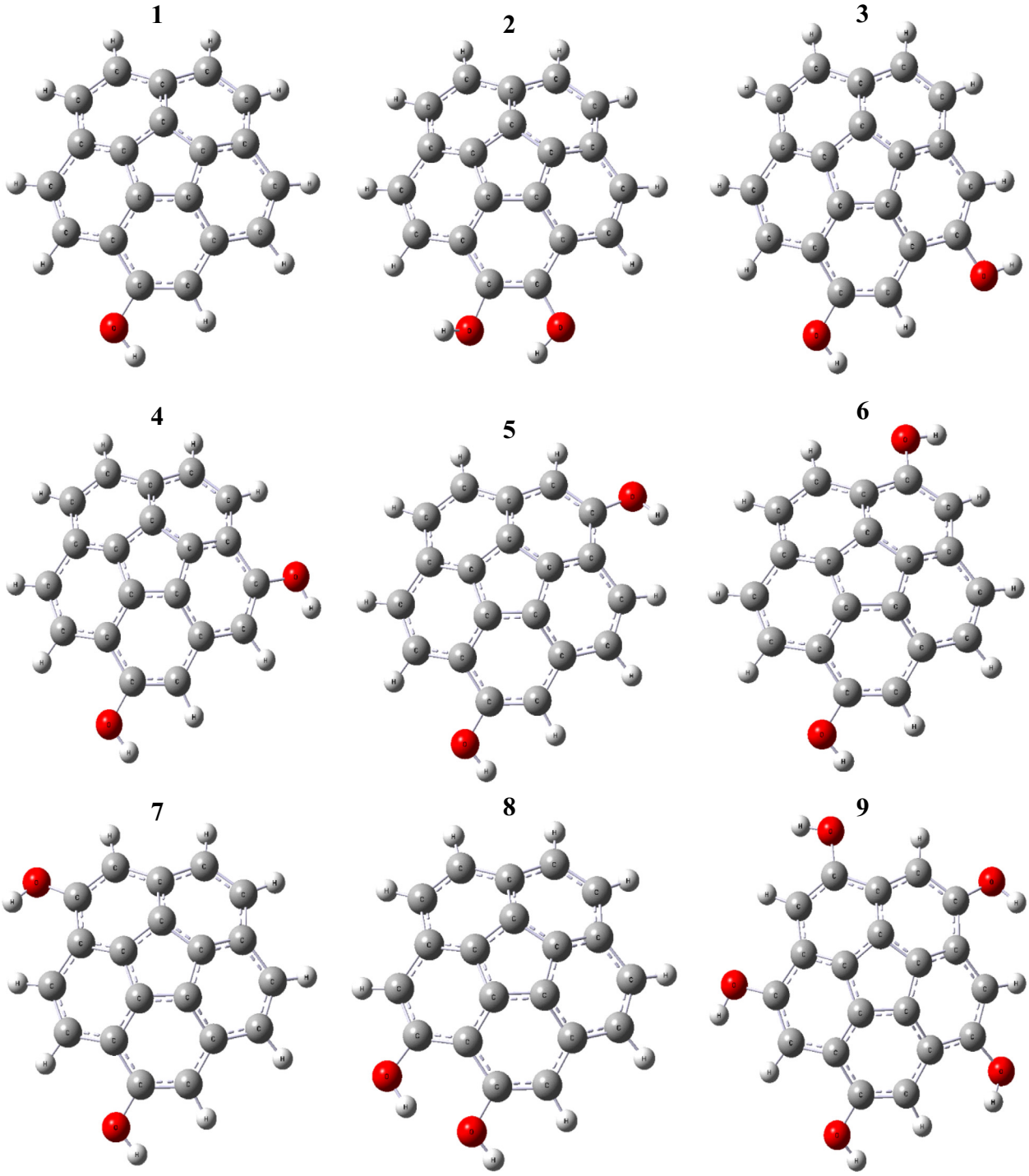

Figure 3 Structures **1**–**9** for hydroxyl derivatives corannulene.

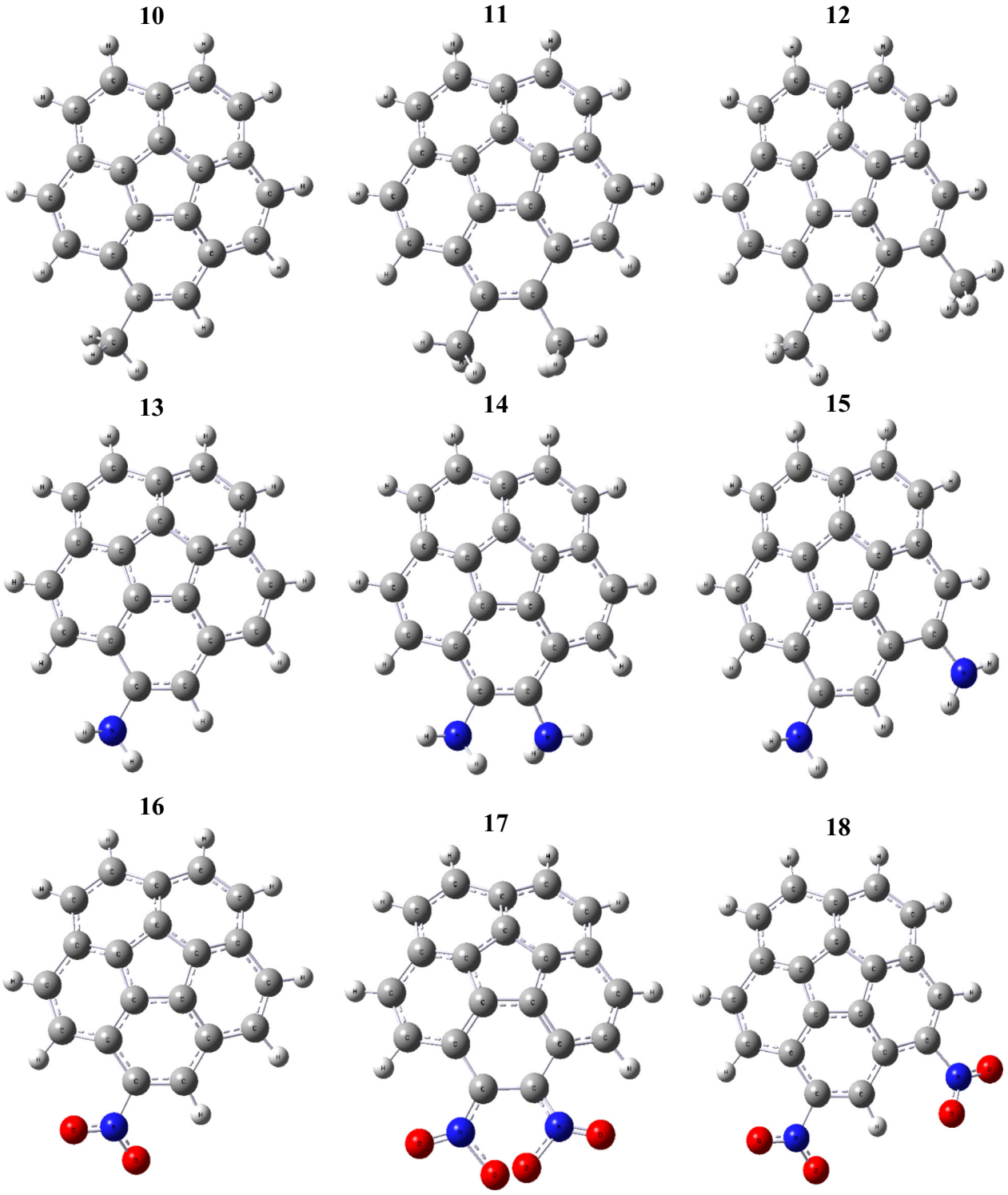

Figure 4 Structures **10**–**12** for methyl, **13**–**15** for amine and **16**–**18** for nitro derivatives corannulene.

and parallel) on the concave and convex sides of corannulene (Figs. 1 and 2) and full geometry optimizations are performed. To obtain the most stable adsorption site of each structure on the corannulene rings, several possible configurations (on pentagonal or each of the hexagonal rings) have been considered and the optimization was carried out. Adsorption of hydrogen in head-on orientation is more stable than in parallel orientation that it is in agreement with Scanlon et al. studies [33], so throughout this study head-on orientation was used. Obtained binding energies for concave/head, concave/parallel, convex/head and convex/parallel orientations of corannulene and hydrogen are −0.91, −0.05, −0.82 and −0.01 kcal/mol, respectively. To make the understanding better, we have collected the calculated values of total energy (Ha), binding energy (kcal/mol) and corrected binding energy (kcal/mol) for corannulene, structures **1** and **2** with concave-convex sides of corannulene

and Head-on or parallel orientation of H_2 at MP2/6-31G(d) level of theory as Supplementary information. In our systematic study, the first model system was the pure corannulene molecule, while the other model systems resulted from the substitution of H atom by the different groups such as –OH, –NO_2, –NH_2 and –CH_3 in the corannulene molecule. The calculations for all of the considered systems in the present study were carried out by using the Gaussian 03 program [15] using the default convergence criteria given in the program. Gauss View 5 program was used for visualization of the results [11].

2.2. Calculation of the binding energy

We have calculated the binding energy of molecular hydrogen with corannulene derivatives. The binding energy for the hydrogen molecule is defined as:

$$BE = E(cmpx) - [E(cor) + E(H_2)] \quad (1)$$

where, E(cmpx) is the energy of the hydrogen-corannulene derivatives complex, E(cor) and E(H_2) are the energies of the corannulene derivative and hydrogen molecules, respectively [1]. It is well known that physisorption energies must be corrected by BSSE. Therefore, we used the counterpoise correction suggested by Boys and Bernardi in 1970 [4]. The counterpoise corrected binding energies were calculated as follows:

$$BE^{CP} = BE + \delta^{BSSE} \quad (2)$$

where, BE^{CP} is the BSSE corrected binding energy, BE is the BSSE uncorrected interaction energy and δ^{BSSE} is the counterpoise correction [8]. The binding energies of the H_2 molecule to both the concave and the convex sides of two structures of OH derivatives of corannulene have been calculated. The results suggested that the hydrogen molecule prefers to bind the corannulene molecule on the concave surface, so for other structures, we have just investigated the binding energy of the H_2 molecule to the concave side.

3. Results and discussion

3.1. Corannulene derivatives

There are three types of carbon atoms in corannulene (Fig. 1): "hub" carbons (C_h), the innermost five carbons on the five-member ring; "rim" carbons (C_r), the outmost 10 carbons bonded to one hydrogen each are named; "bridge" carbons (C_b), the remaining five carbons connecting between the rim and hub carbon atoms [32]. The calculation shows that rim carbon atoms possess higher electron density than hub and bridge carbon atoms. We have substituted corannulene peripheral H atoms by OH groups. Nine hydroxyl derivatives were considered. Seven of them were related to substitution of two peripheral H atoms with OH groups (structures **2**–**8**) and two structures were related to the substitution of one and five H atoms with OH groups, respectively (structures **1** and **9**). These structures are presented in Fig. 3.

Moreover, we have also substituted the corannulene peripheral H atoms with –CH_3, –NH_2 and –NO_2 groups (presented in Fig. 4) and investigated the effect of these substituent groups on hydrogen adsorption. We have considered three structures for each of these groups. A structure was related to the substitution of one H atom with these groups (structures **10**, **13** and **16**) and two structures were related to substitution of two H atoms with these groups. One of them is substitution of two hydrogen atoms joined to the rim carbon of a ring (structures **11**, **14** and **17**) and the other is substitution of two hydrogen atoms joined to the alternate rim carbon of two adjacent rings (structures **12**, **15** and **18**) with –CH_3, –NH_2 and –NO_2 groups.

Table 1 Type and number of substituent group, total energy (Hartree), binding energy (kcal/mol), BSSE corrected binding energy(kcal/mol), H–L energy gap (eV) and dipole moment (Debye) of the corannulene derivatives (presented in Figs. 3 and 4) at MP2/6-31G(d) level of theory.

Structure	Substituent	Total energy	Binding energy	Corrected binding energy	H–L energy gap	μ
$C_{20}H_{10}$	–	−765.73	−0.91[a]	−0.32	9.57	2.17[b]
1	OH	−840.76	−0.92	−0.33	9.23	2.65
2	2(OH)	−915.80	−0.92	−0.33	9.05	2.20
3	2(OH)	−915.80	−1.02	−0.12	9.17	3.16
4	2(OH)	−915.80	−0.99	−0.11	9.17	3.27
5	2(OH)	−915.79	−0.83	−0.27	9.07	2.96
6	2(OH)	−915.80	−0.94	−0.34	8.93	3.38
7	2(OH)	−915.79	−1.01	−0.07	9.18	2.76
8	2(OH)	−915.80	−0.75	−0.27	8.96	3.87
9	5(OH)	−1140.90	−0.97	−0.10	9.23	4.51
10	CH_3	−804.90	−0.93	−0.34	9.42	2.22
11	2(CH_3)	−844.07	−0.21	−0.05	9.31	2.28
12	2(CH_3)	−844.07	−0.15	−0.04	9.38	2.28
13	NH_2	−820.92	−1.07	−0.25	9.01	1.87
14	2(NH_2)	−876.12	−0.12	−0.11	8.61	2.24
15	2(NH_2)	−876.12	−0.05	−0.05	8.86	3.15
16	NO_2	−969.74	−0.91	−0.12	8.92	6.12
17	2(NO_2)	−1173.62	−0.08	−0.08	7.64	7.11
18	2(NO_2)	−1173.74	−0.11	–0.10	8.76	9.48

[a] Reported value in [33] is −0.94.
[b] Reported value in [38] is 2.18 at the level of B3LYP/6-311G(d,p) and in [33] is 2.15 at the level of MP2/6-31G(d).

3.2. Binding energy

Type and number of the substituent group, total energy, interaction energy with the hydrogen molecule, BSSE corrected energy, H–L energy gap and dipole moment of the corannulene and its derivatives at MP2/6-31G(d) level of theory have been collected in Table 1.

We first considered the optimization of a hydrogen molecule on the concave and the convex sides of clean corannulene molecules by employing the MP2/6-31G(d) level of theory. The results showed that binding energies of −0.91 and −0.82 kcal/mol with the hydrogen molecule oriented perpendicularly on the concave and convex sides, respectively. These results are in good agreement with the values suggested by Scanlon et al. at the MP2/6-31G(d) level of theory, they have obtained −0.94 and −0.83 kcal/mol at 298 K and 1 atm, respectively [33]. Also, the effect of the BSSE correction on the binding energies has been considered and the values −0.32 and −0.31 kcal/mol have been obtained for the concave and convex sides of corannulene, respectively.

In corannulene hydroxyl derivatives, structures **1**, **2** and **6** have more and the other structures have less binding energy than intact corannulene. The electronic density, charge transfer and spatial prohibition of the substituted groups affects the binding energy. Also, the binding energy varies depending upon the site and side of absorption. Comparison of the value of binding energy of structures **2**–**8** in Table 1 indicates the type, number and position of the substituent group effects on the charge transfer and binding energy. In the structures **4** and **6**, charge transfer for both substituent groups is the same, but their position is different that leads to various binding energies.

The results in Table 1 demonstrated that the increment of the electronic density because of substitution of electron donor groups facilitates hydrogen adsorption, thus the substitution of the peripheral H atoms by electron donor groups leads to larger binding energies than when H atoms are substituted by electron acceptor groups. Comparison of the BSSE corrected binding energy of the structures $C_{20}H_{10}$, **1**, **10**, **13** and **16** confirmed it.

The H–L energy gap in Table 1 has been used as a measure of kinetic stability and reactivity. A large gap indicates that it is difficult to add electrons to a high LUMO and remove electrons from deep HOMO [10]. For evaluation of the stability of considered structures, the results in Table 1 show that generally, substitution of H atoms with each of the considered

Table 2 The values of the Mulliken atomic charges for (C_{rim}), all atoms in substituent groups, all substituent groups and total Mulliken charge transfer of the substituent groups for each structure.

Structure	C_{rim}	C_1	O_1	O_2	N	H_1	H_2	H_3	Substituent	Total charge transfer
1	0.416	–	−0.757	–	–	0.460	–	–	−0.297	−0.297
2	0.368	–	−0.771	–	–	0.489	–	–	−0.282	−0.615
	0.250	–	−0.796	–	–	0.463	–		−0.333	
3	0.412	–	−0.759	–	–	0.461	–	–	−0.298	−0.599
	0.410	–	−0.761	–	–	0.460	–	–	−0.301	
4	0.421	–	−0.756	–	–	0.460	–	–	−0.296	−0.592
	0.421	–	−0.756	–	–	0.460	–	–	−0.296	
5	0.419	–	−0.756	–	–	0.461	–	–	−0.295	−0.593
	0.410	–	−0.760	–	–	0.462	–	–	−0.298	
6	0.412	–	−0.759	–	–	0.459		–	−0.300	−0.600
	0.412	–	−0.759	–	–	0.459	–	–	−0.300	
7	0.415	–	−0.757	–	–	0.461	–	–	−0.296	–0.592
	0.406	–	−0.759	–	–	0.463	–	–	−0.296	
8	0.432	–	−0.803	–	–	0.472	–	–	−0.331	–0.608
	0.435	–	−0.783	–	–	0.506	–	–	−0.277	
9	0.413	–	−0.760	–	–	0.462	–	–	−0.298	–1.483
	0.415	–	−0.755	–	–	0.461	–	–	−0.294	
	0.399	–	−0.759	–	–	0.465	–	–	−0.294	
	0.395	–	−0.760	–	–	0.461	–	–	−0.299	
	0.414	–	−0.758	–	–	0.460	–	–	−0.298	
10	0.048	−0.514	–	–	–	0.177	0.180	0.178	0.021	0.021
11	0.012	−0.519	–	–	–	0.177	0.180	0.180	0.018	0.035
	0.011	−0.521	–	–	–	0.177	0.179	0.182	0.017	
12	0.048	−0.514	–	–	–	0.176	0.177	0.179	0.018	0.036
	0.048	−0.514	–	–	–	0.176	0.177	0.179	0.018	
13	0.288	–	–	–	−0.882	0.360	0.363	–	−0.159	−0.159
14	0.209	–	–	–	−0.896	0.357	0.381	–	−0.158	−0.337
	0.190	–	–	–	−0.912	0.365	0.368	–	−0.179	
15	0.285	–	–	–	−0.882	0.361	0.361	–	−0.160	−0.315
	0.262	–	–	–	−0.875	0.359	0.361	–	−0.155	
16	0.148	–	−0.455	−0.459	0.465	–	–	–	−0.449	−0.449
17	0.280	–	−0.500	−0.179	0.268	–	–	–	−0.411	−0.808
	0.260	–	−0.503	−0.177	0.283	–	–	–	−0.397	
18	0.158	–	−0.454	−0.445	0.464	–	–	–	−0.435	−0.872
	0.163		−0.451	−0.452	0.466	–	–	–	−0.437	

groups leads to decreasing of the gap and so decreasing of the kinetic stability and increasing of the reactivity. Our results are in good agreement with Santos et al. results [32]. Comparison of the H–L energy gap of the structures **1**, **10**, **13** and **16** with only a functional group indicated that effect of substituent group type decreases in order of: NO_2 > NH_2 > OH > CH_3. Comparison of the H–L energy gap of the structures **2**, **11**, **14** and **17** and the structures **3**, **12**, **15** and **18** with two functional groups in similar positions is exactly in the above order, respectively.

To understand the reactivity of the molecules in their ground states there are some reactivity indices used in the literature [14,37]. The electronic chemical potential (μ) describes the changes in the electronic energy with respect to the number of electrons; the chemical hardness (η) and the global electrophilicity (ω), measures the stabilization in energy when the system acquires an additional electronic charge from the environment. Recently, Domingo et al. introduced a nucleophilicity index (N), which allows the behavior of the nucleophilic species to be assessed [13]. The values of the chemical hardness (η) for structures **1**, **10**, **13** and **16** are 0.33927, 0.34622, 0.33147 and 0.32808, respectively that is in good agreement with obtained results from the H–L gap energy for the kinetic stability and reactivity.

3.3. Charge transfer

The values of the Mulliken atomic charges for carbon atoms bonded to substituent groups (C_r), all atoms in substituent groups, all substituent groups and total Mulliken charge transfer of the substituent groups for each structure were collected in Table 2. In all considered structures, dipole moment is more than corannulene except in structure **13**. It is expected that with increment of the dipole moment of the structures, induced-dipole moment in hydrogen molecule and so binding energy increases but the results in Tables 1 and 2 did not show any relationship between them. We can say moreover dipole moment, spatial prohibition and other factors affect the binding energy and all of them must be considered simultaneously.

4. Conclusions

We have substituted the peripheral H atoms in the corannulene molecule as a carbon nanostructure by OH, CH_3, NH_2 and NO_2 groups and their molecular hydrogen physisorption was evaluated at MP2/6-31G(d) level of theory. Two orientations of hydrogen were used on the concave and convex sides of corannulene so that binding to the concave face is favored relative to the convex face. The average binding energy was calculated and corrected for the BSSE using the counterpoise method. Results showed that binding energy varies depending upon the type and number of substituent groups and also the site and side of absorption.

The increment of the electronic density because of substitution of electron donor groups facilitates hydrogen adsorption and leads to larger binding energies than when H atoms are substituted by electron acceptor groups. Substitution of H atoms with each of the considered groups leads to decreasing of the H–L energy gap and so decreasing of the kinetic stability and increasing of the reactivity. The H–L energy gap of the corannulene derivatives decreases in the order of: CH_3 > OH > NH_2 > NO_2. Therefore, corannulene derivatives are more reactive than intact corannulene. Also, the results concluded that the structures with one methyl substituted and some of the hydroxyl derivatives are the best and the structures with NO_2 substituted are the worst structures for hydrogen adsorption. In all structures of corannulene derivatives, dipole moment is more than corannulene except in one structure.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jscs.2014.02.003.

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